ISSN 1063-7834, Physics of the Solid State, 2013, Vol. 55, No. 10, pp. 2108–2115. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © M.G. Kostenko, A.V. Lukoyanov, A.A. Rempel, 2013, published in Fizika Tverdogo Tela, 2013, Vol. 55, No. 10, pp. 1993–1999.

PHASE TRANSITIONS

Electronic Structure and Stability of Nonstoichiometric Titanium Monoxide TiO_y with Structural Vacancies in One of the Sublattices

M. G. Kostenko[a], A. V. Lukoyanov[b, c], and A. A. Rempel[a, c, *]

[a] *Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, ul. Pervomaiskaya 91, Yekaterinburg, 620990 Russia*

[b] *Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, ul. Sofii Kovalevskoi 18, Yekaterinburg, 620219 Russia*

[c] *Ural Federal University named after the first President of Russia B. N. Yeltsin (Ural State Technical University—UPI), ul. Mira 19, Yekaterinburg, 620002 Russia*

* *e-mail: rempel@ihim.uran.ru*

Received April 2, 2013

Abstract—The electronic structure of nonstoichiometric titanium monoxide TiO_y with different compositions y, which contains structural vacancies either in the metallic sublattice or in the nonmetallic sublattice, has been investigated using the supercell method within the DFT-GGA approximation with pseudopotentials. The cases of ordered and disordered arrangements of vacancies have been considered. It has been found that the complete removal of vacancies from the sublattice is energetically unfavorable, and the ordering of oxygen vacancies according to the type of the $Ti_6O_5\square_1$ superstructure, as well as titanium vacancies according to the $Ti_5\blacksquare_1O_6$ type, does not lead to the stabilization of the $B1$ basic structure of titanium monoxide.

DOI: 10.1134/S106378341310017X

1. INTRODUCTION

In the majority of binary compounds of transition metals, nonstoichiometry is realized due to the replacement of atoms of one of the sublattices by structural vacancies [1]. In titanium monoxide TiO_y, structural vacancies are contained simultaneously in two sublattices [2–4]. If the compound has the equiatomic composition ($y = 1$), the content of vacancies is approximately equal to 15 at % in each sublattice [2–4]. When the composition deviates from stoichiometric, the content of vacancies increases in one of the sublattices and decreases in the other. In order to show the existence of vacancies in both sublattices of titanium monoxide, it is usual to use the formula Ti_xO_z or $Ti_x\blacksquare_{1-x}O_z\square_{1-z}$, where x and z are the fractions of atomic positions in the titanium and oxygen sublattices, respectively; ■ and □ are structural vacancies in these sublattices. The composition y, which is specified in the formula TiO_y, is equal to z/x. Owing to the high content of structural vacancies, the composition y of titanium monoxide varies over a wide range from 0.70 to 1.25 [2].

Titanium monoxide has a basic structure of the $B1$ (NaCl) type. Vacancies can be located in sites of the sublattices either without a long-range order or in an ordered manner. If the vacancies are arranged randomly, the structure retains the cubic symmetry of the $B1$ basic structure [2, 3, 5]. The cubic phase with a disordered arrangement of vacancies is in thermodynamic equilibrium at temperatures above 1263 K [2]. During a slow annealing below 1263 K, there occurs a redistribution of vacancies over sites of the sublattices of the basic structure, which results in the formation of ordered phases [2, 3, 5, 6]. For titanium monoxide with the stoichiometric composition ($y = 1.0$), the ordering leads to the formation of the ordered monoclinic phase Ti_5O_5 ($Ti_5\blacksquare_1O_5\square_1$) with the unit cell shown in Fig. 1. Each sublattice of the $B1$ basic structure of the ordered phase contains 1/6 of vacant sites.

Theoretical investigations of the electronic structure, as well as calculations of the total energy and the enthalpy of formation of titanium monoxide, which are presented in [7–12], have demonstrated that the ordered structure $Ti_5\blacksquare_1O_5\square_1$ is energetically more favorable as compared to the disordered structure. The stabilization of the $B1$ basic structure manifests itself both as a significant change of the $3d$ electronic states of titanium atoms surrounding the oxygen vacancy [10, 12] and as a decrease of the Madelung energy due to the ordering of vacancies [7, 8, 10].

The annealing of titanium monoxide at high pressures and temperatures makes it possible to decrease the content of vacancies down to their complete removal from the compounds [13, 14]. According to Taylor and Doyle [13], the zero concentration of vacancy can be achieved by annealing at a temperature of 1650 K and a pressure of 77.4 kbar. Bartkowski et al. [14] synthesized samples of vacancy-free titanium monoxide at a temperature of 1938 K and a pressure of 80.0 kbar. The theoretical study performed by Anders-

son et al. [9] demonstrated that the titanium monoxide phase with the complete absence of vacancies should be in thermodynamic equilibrium only at high pressures; however, it is known that this phase is also stable under normal conditions [13, 14]. Therefore, a change in the concentration of vacancies, along with the change in stoichiometry and with the ordering, can be used to purposefully control the properties of the compound, which extends the region of its practical applications.

Titanium monoxide without vacancies should have a perfect $B1$-type structure and a stoichiometric composition. At the same time, the disordered cubic phase TiO_y has a very wide homogeneity region with the lower boundary lying in the range of 0.7–0.9 and the upper boundary in the range of 1.25–1.33 [2–6, 15]. The homogeneity region of the ordered monoclinic phase Ti_5O_5 ($Ti_5\blacksquare_1O_5\square_1$), according to the data reported by Watanabe et al. [2], lies in the range from 0.9 to 1.1, but according to the data presented by Murray and Wriedt [15], it is completely absent. In the presence of a nonstoichiometry, structural vacancies should be contained in at least one of the sublattices of the $B1$ basic structure.

It is known that experiments on the decrease in the concentration of vacancies in titanium monoxide were carried out only on samples of stoichiometric composition. Since the possibility of varying the concentration of vacancies in both the titanium sublattice and the oxygen sublattice exists for the disordered phase at normal pressure, it can be assumed that the same possibility will also continue to exist in titanium monoxide at a high pressure, when the concentration of vacancies in both sublattices is decreased to the minimum possible level.

In the disordered cubic phase with a deviation from stoichiometry, the concentration of vacancies increases in one of the sublattices and decreases in the other [4]. If there are no vacancies in one of the sublattices, the change in the composition of titanium monoxide can occur only by varying the concentration of vacancies in the other sublattice. It is reasonable to assume that the high-temperature annealing at high pressures for samples of nonstoichiometric composition should lead to the removal of vacancies from only one sublattice. Such a behavior of structural vacancies has not been considered previously. Theoretical studies on simulation and calculation of the energy parameters for a possible structure of the high-pressure phase of nonstoichiometric compositions have also not been performed.

The electronic structure and stability of the disordered cubic phase of titanium monoxide with different compositions were investigated in [11, 16]. In our recent work [11], it was shown that the stability of the phase increases with an increase in the oxygen concentration, and conclusions were drawn about the influence of different concentrations of vacancies in the metallic and nonmetallic sublattices of the $B1$ basic structure of titanium monoxide. An increase in the concentration of vacancies in the oxygen sublattice and a decrease in their concentration in the titanium sublattice lead to a local decrease in the density of states at the Fermi level due to the redistribution of Ti $3d$ states, whereas a decrease in the concentration of oxygen vacancies and an increase in the concentration of titanium vacancies significantly decrease the Fermi energy. In this respect, the investigation of the electronic structure and total energy of the high-pressure phase is interesting in that it will provide a means for elucidating the influence of vacancies in only one sublattice with their complete absence in the other sublattice over the entire homogeneity region of the compound.

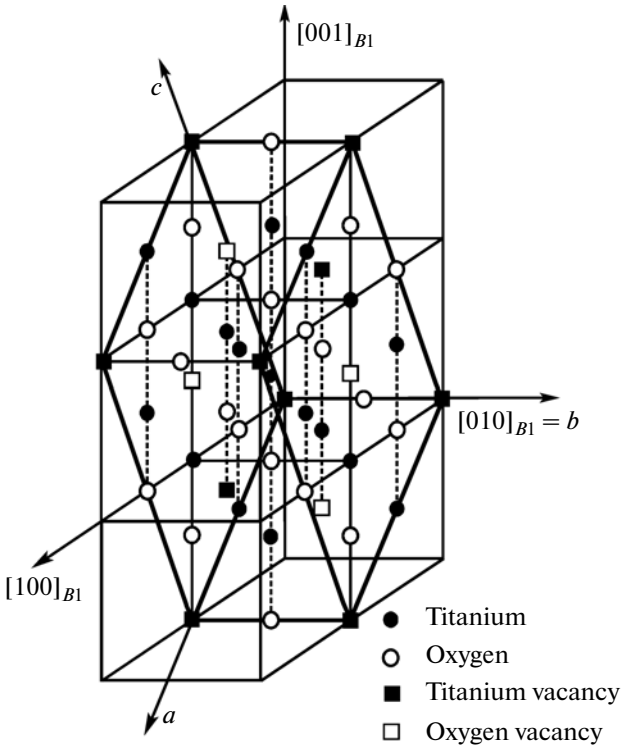

Fig. 1. Unit cell of the $Ti_5\blacksquare_1O_5\square_1$ superstructure [1, 2, 5]. The axes a, b, and c of the superstructure and the directions of the $B1$ basic structure are shown.

The purpose of this work was to elucidate the influence of vacancies in the titanium and oxygen sublattices on the electronic structure and stability of the high-pressure phase of titanium monoxide of substoichiometric ($y < 1.0$) and superstoichiometric ($y > 1.0$) compositions both with an ordered arrangement and with a disordered arrangement of vacancies.

2. CALCULATION METHOD

The theoretical study of the electronic structure and calculations of the total energy were performed in

the framework of the density functional theory (DFT) [17, 18] using the exchange–correlation potential of the generalized gradient approximation (GGA) correction in Perdew–Burke–Ernzerhof (PBE) version [19]. All the self-consistent calculations were carried out using the plane wave pseudopotential approach implemented in the QUANTUM ESPRESSO software package [20]. The kinetic energy of plane waves did not exceed 45 Ry. In addition to the valence levels, the pseudopotential of titanium included the core 3*s*3*p* states. The calculations were performed on the "Uran" supercomputer at the Institute of Mathematics and Mechanics of the Ural Branch of the Russian Academy of Sciences (Yekaterinburg, Russia).

In order to take into account the disorder in the arrangement of vacancies in the calculations of the electronic structure, we used the supercell method. The supercell was constructed by a twofold translation of the unit cell of the ordered monoclinic phase Ti_5O_5 along the crystallographic directions *a* and *b*. It contained 96 sites of the *B*1 basic structure. The ordered state was simulated by placing vacancies only in the sites corresponding to sites of the sublattices of vacancies in the ordered monoclinic phase. It is clear that the complete ordering is possible only for the compositions $y = 5/6$ and 6/5. This case corresponds to the hypothetical superstructures $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$, which were considered in [9]. As the index *y* increases from 5/6 to 1, the concentration of oxygen vacancies in $Ti_6O_5\square_1$ decreases to zero. Similarly, the titanium sublattice in $Ti_5\blacksquare_1O_6$ is filled with atoms to 100% with a decrease in the index *y* from 6/5 to 1. It is assumed that the atoms which appear in the sublattices of vacancies in the ranges $5/6 < y < 1$ and $1 < y < 6/5$ are arranged randomly in the corresponding sublattices; i.e., the sublattices of vacancies become disordered. Therefore, in the investigation of the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ superstructures, we also used the supercell method. For each chosen composition *y*, we constructed ten supercells with a random arrangement of vacancies either in the titanium sublattice or in the oxygen sublattice of the *B*1 basic structure, or only in the sublattices of titanium vacancies or oxygen vacancies of the $Ti_5\blacksquare_1O_5\square_1$ superstructure in the case of $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$. The results of the calculations for ten supercells were averaged. Since the appearance of vacancies can cause a displacement of atoms with respect to the sites of the basic structure, in all cases we carried out the relaxation of atomic positions.

The enthalpy of formation was calculated using the formula

$$\Delta H_{TiO_y} = k\left(E_{TiO_y} - N_{Ti}E_{Ti} - \frac{1}{2}N_O E_{O_2}\right)/N \text{ [kJ/mol]}, \quad (1)$$

where *k* is the coefficient of conversion into kJ/mol; E_{TiO_2} is the total energy of titanium monoxide per cell (or per supercell for TiO_y); N_{Ti} and N_O are the numbers of titanium and oxygen atoms in the cell (supercell), respectively; E_{Ti} is the total energy of metallic titanium per atom; E_{O_2} is the total energy of the oxygen molecule with inclusion of the effect of spin-polarization; and *N* is the number of structural units in the cell (supercell). If it needs to compare the enthalpies of formation of the phases of stoichiometric compositions, the structural unit should be taken as the Ti–O pair; then we obtain $N = 40$. In the analysis of the influence of one of the phases, we should use the structural unit $Ti_x\blacksquare_{1-x}O_z\square_{1-z}$ or TiO_y. In this case, the value of *N* is always equal to 48 or to the number of titanium atoms in the supercell. Different phases of the same composition *y* may contain different concentrations of vacancies in the sublattices. Therefore, if it needs to compare the stabilities of different phases of the same composition *y*, the structural unit should be considered only as TiO_y; then the value of *N* will be equal to the number of titanium atoms in the supercell.

3. DEPENDENCE OF THE LATTICE CONSTANT AND FRACTION OF ATOMIC POSITIONS IN SUBLATTICES ON THE COMPOSITION

Changes in the concentration of vacancies in the titanium and oxygen sublattices affect the lattice constant of the *B*1 basic structure. The lattice constant is equal to 418.2 pm for the disordered cubic phase and 414.2 pm for the ordered monoclinic phase [5]. The dependence of the lattice constant on the composition was experimentally investigated only for the disordered cubic phase [21, 22]. The data obtained in [22] are approximated by the linear relationship

$$a = 424.5 - 6.4y \text{ [pm]}. \quad (2)$$

It is assumed that the dependence of the lattice constant on the composition for the ordered monoclinic phase can be described by the equation of a straight line with the same slope. In this case, over the entire homogeneity region, the difference in the lattice constants of the *B*1 basic structure for the ordered monoclinic and disordered cubic phases is equal to 4 pm. Both dependences are shown by lines *1* and *2* in Fig. 2.

The concentrations of vacancies in the sublattices as functions of the composition were experimentally investigated in [4, 21, 22]. Based on these data, it was proposed in [8] to use approximate linear dependences (lines *1*, *2* and *3*, *4* in Fig. 3). The homogeneity region taken for the calculations in [8, 11] lies in the range from 0.75 to 1.33. The concentration of vacancies at the boundaries of the homogeneity region should reach 25% in one of the sublattices and vanish in the other. The difference between the high-pressure phase and the disordered cubic phase lies in the fact that, in the former case, the deviation from the stoichiometric composition will not lead to a change in the concentration of vacancies in one of the sublattices

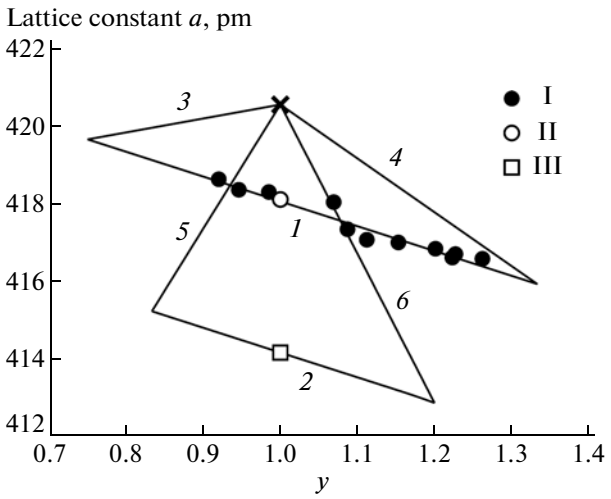

Fig. 2. Dependence of the lattice constant on the composition of titanium monoxide TiO_y: (I) experimental data for the disordered phase [22] (these data are approximated by the equation of straight line *1*), (II) lattice constant of the disordered phase, and (III) lattice constant of the basic structure of the ordered phase (parameter b of the monoclinic unit cell in Fig. 1) of stoichiometric composition according to [2]. (*2*) Proposed dependence for the ordered monoclinic phase $Ti_5\blacksquare_1O_5\square_1$; (*3*, *4*) proposed dependences for the high-pressure phase with a disordered arrangement of vacancies; and (*5*, *6*) similar dependences for the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ superstructures, respectively.

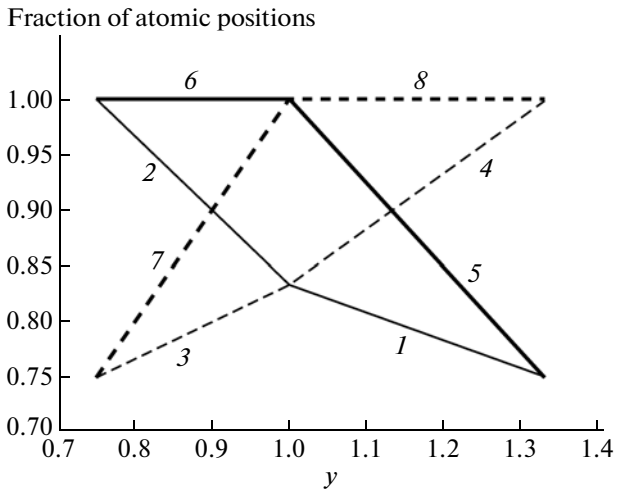

Fig. 3. Dependence of the fraction of atomic positions in the sublattices on the composition of titanium monoxide TiO_y: (*1*–*4*) approximate linear dependences for the disordered cubic phase and (*5*–*8*) hypothetical dependences for the high-pressure phase. Solid and dashed lines correspond to the titanium and oxygen sublattices, respectively.

(lines *5*, *6* and *7*, *8* in Fig. 3). The sublattice of titanium vacancies in the $Ti_5\blacksquare_1O_6$ superstructure, as well as the sublattice of oxygen vacancies in the $Ti_6O_5\square_1$ superstructure, corresponds to no more than 1/6 (16.7%) of the sites in one of the sublattices of the $B1$ basic structure, while vacancies in the other sublattice are absent. Therefore, the homogeneity region of the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ superstructures is narrower than the homogeneity region of the disordered cubic phase (Fig. 3).

The disordered cubic phase at the boundaries of the homogeneity region is identical in the concentration of vacancies to the high-pressure phase (Fig. 3); therefore, both phases should have the same lattice constant. The experimentally determined lattice constant of the high-pressure phase of stoichiometric composition, for which there are no vacancies in both sublattices, is equal to 420.6 pm. When experimental data for nonstoichiometric compositions are not available, we should use a linear dependence of the lattice constant on the composition for one of the sublattices (lines *3* and *4* in Fig. 2). A similar assumption should be made in the case of an ordered arrangement of vacancies (lines *5* and *6* in Fig. 2). Thus, all the calculations were carried out using the model dependences of the lattice constant and the concentration of vacancies on the composition (Figs. 2 and 3).

The number of atoms and vacancies in the supercell as a function of the composition is presented in the table. The calculations were performed for all compositions in the case of a disordered arrangement of vacancies and only for the compositions in the region from $y = 40/48$ to 48/40 in the case of the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ superstructures.

4. ELECTRONIC STRUCTURE

Figure 4 shows the electron densities of states for titanium monoxide without vacancies (Fig. 4a), the ordered monoclinic phase (Fig. 4b), and the disordered cubic phase (Fig. 4c) according to the data obtained in [11]. Figure 5 presents the electron densities of states calculated in this work for the high-pressure phase of substoichiometric (Fig. 5a) and superstoichiometric (Fig. 5b) compositions. Figure 6 shows the electron densities of states for the hypothetical superstructures $Ti_6O_5\square_1$ (Fig. 6a) and $Ti_5\blacksquare_1O_6$ (Fig. 6b) of different stoichiometric compositions. The composition $y = 40/48$ (40 oxygen atoms and 48 titanium atoms in the supercell) corresponds to the completely ordered superstructure $Ti_6O_5\square_1$, and the composition $y = 48/40$ (48 oxygen atoms and 40 titanium atoms in the supercell), to the completely ordered superstructure $Ti_5\blacksquare_1O_6$.

In all the considered cases, the low-energy part of the band of occupied states is formed predominantly by the O $2p$ states, and the high-energy part of this band is formed primarily by the Ti $3d$ states. The high-pressure phase of stoichiometric composition (vacations are completely absent) has the highest density of states at the Fermi level, whereas the ordered monoclinic phase $Ti_5\blacksquare_1O_5\square_1$ is characterized by the lowest density of states due to the presence of the pseudogap. A disordering of vacancies substantially decreases the

Number of atoms and vacancies in the supercell

y	Number of atoms in the titanium sublattice	Number of vacancies in the titanium sublattice	Number of atoms in the oxygen sublattice	Number of vacancies in the oxygen sublattice
36/48	48	0	36	12
38/48	48	0	38	10
40/48	48	0	40	8
42/48	48	0	42	6
44/48	48	0	44	4
46/48	48	0	46	2
48/48	48	0	48	0
48/46	46	2	48	0
48/44	44	4	48	0
48/42	42	6	48	0
48/40	40	8	48	0
48/38	38	10	48	0
48/36	36	12	48	0

pseudogap and increases the density of states at the Fermi level. With an increase in the concentration of vacancies in the oxygen sublattice of the high-pressure phase (Fig. 5a), the depth of the pseudogap increases. On the other hand, an increase in the fraction of vacancies in the titanium sublattice in the case when they are absent in the oxygen sublattice does not lead to the appearance of a similar dip in the density of states near the Fermi level (Fig. 5b). According to the data reported in [11], a dip appears in the density of states for the disordered cubic phase of the same compositions when a certain fraction of vacancies remains in the oxygen sublattice.

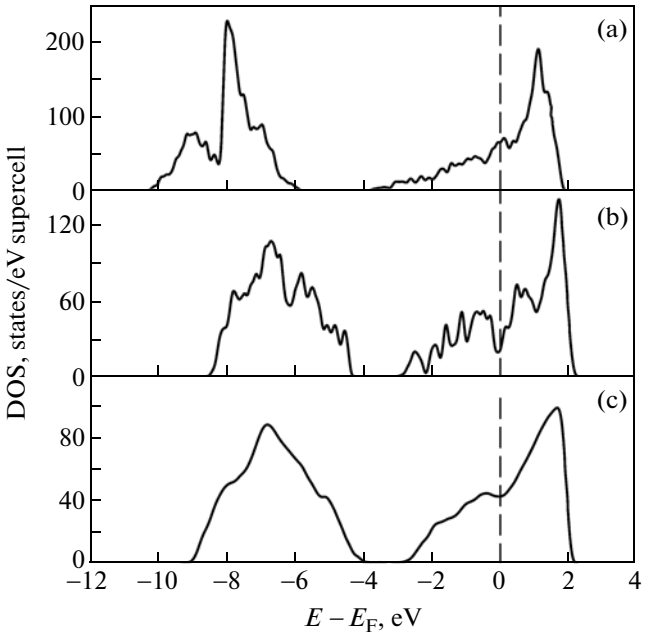

Fig. 4. Electron densities of states of (a) titanium monoxide without vacancies, (b) ordered monoclinic phase $Ti_5\blacksquare_1O_5\square_1$, and (c) disordered cubic phase of stoichiometric composition [11]. The Fermi level E_F is indicated by the dashed line.

The appearance of the pseudogap at the Fermi level indicates a redistribution of Ti 3*d* states due to the strengthening of the covalent bonds between the titanium atoms near oxygen vacancies. This mechanism was thoroughly considered in [10] for the ordered monoclinic phase $Ti_5\blacksquare_1O_5\square_1$. The results of our work have demonstrated that the appearance of a dip in the density of states at the Fermi level is possible even in the absence of vacancies in the titanium sublattice, but it is not transformed into a full pseudogap such as in $Ti_5\blacksquare_1O_5\square_1$. It should be noted that the considered effect is revealed only for the disordered phase and, in this case, the ordering of oxygen vacancies according to the type of the $Ti_5O_5\square_1$ superstructure (Fig. 6a) does not lead to a decrease in the density of states directly at the Fermi level. This fact suggests that the effect caused by the ordering of oxygen vacancies according to the type of the $O_5\square_1$ superstructure, which was considered in [10], will take place only with the simultaneous ordering of titanium vacancies according to the type of the $Ti_5\blacksquare_1$ superstructure, i.e., with the formation of the monoclinic phase $Ti_5\blacksquare_1O_5\square_1$.

5. ENTHALPY OF FORMATION

Figure 7 shows the dependences of the enthalpy of formation and the Fermi energy on the composition of the high-pressure phase with a disordered arrangement of vacancies. Similar dependences for the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ superstructures are presented in Fig. 8. In both cases, the stability of titanium monox-

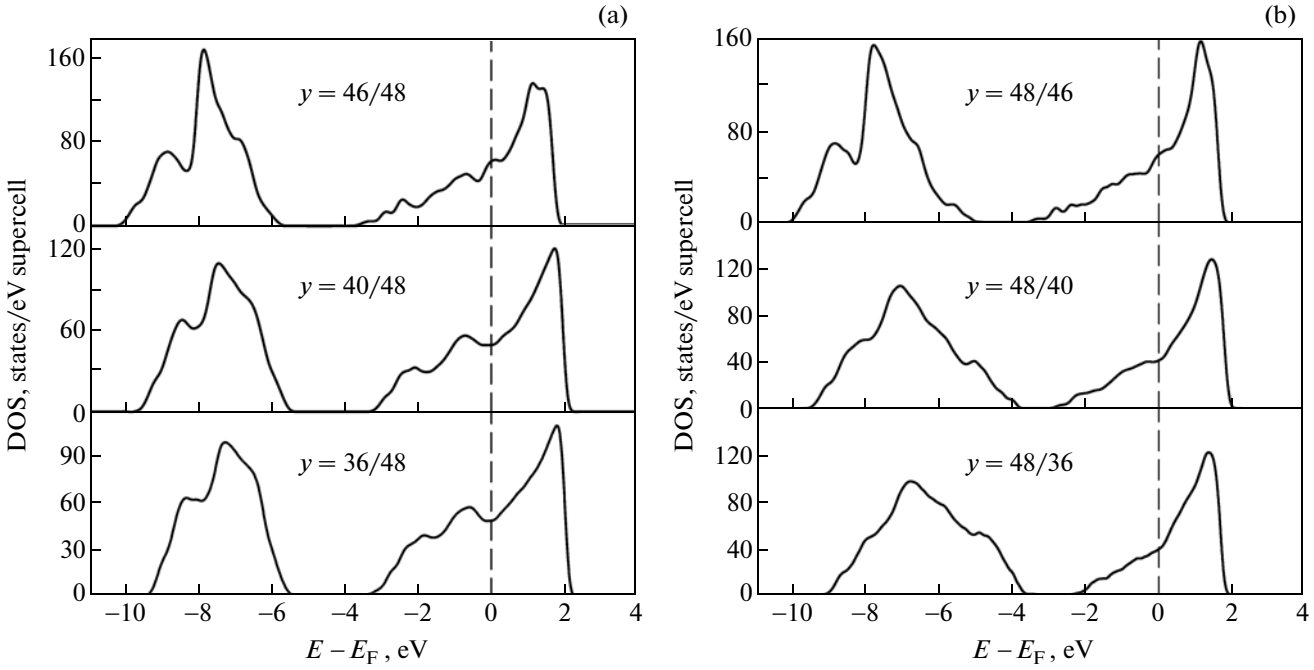

Fig. 5. Electron densities of states as functions of the composition, calculated for the high-pressure phase with a disordered arrangement of structural vacancies in the case of (a) substoichiometric and (b) superstoichiometric compositions. The Fermi level E_F is indicated by the dashed line.

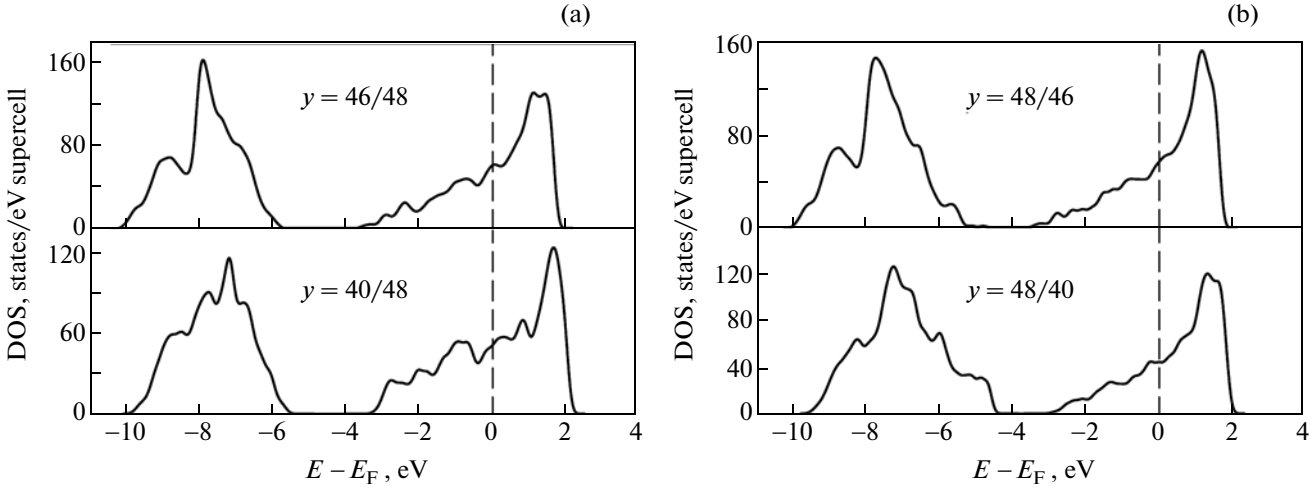

Fig. 6. Electron density of states as functions of the composition, calculated for (a) $Ti_6O_5\square_1$ and (b) $Ti_5\blacksquare_1O_6$ superstructures. The Fermi level E_F is indicated by the dashed line.

ide increases with an increase in the oxygen concentration. For comparison, Fig. 7 shows the data obtained in [11] for the disordered cubic phase. Over the entire homogeneity region of titanium monoxide, the disordered cubic phase at sufficiently low temperatures and pressures is energetically more favorable than the high-pressure phase. The largest difference in the enthalpies of formation is observed in the case of stoichiometric compositions. It is equal to 23.7 kJ/mol and accounts for 4.8% of the enthalpy calculated for vacancy-free TiO (high-pressure phase of stoichiometric composition). With an increase in the distance from the point $y = 1.0$, this difference decreases to zero. In the model accepted in the present study, the high-pressure phase at $y = 0.75$ and 1.33 is equivalent to a disordered cubic phase of the same compositions. Consequently, at the boundaries of the homogeneity

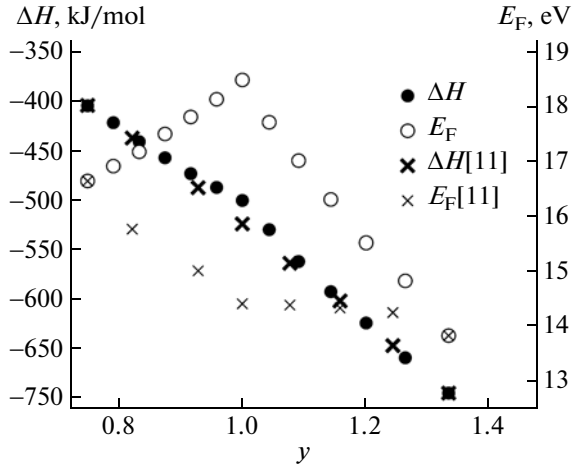

Fig. 7. Dependences of the enthalpy of formation and the Fermi energy on the composition y for the high-pressure phase with a disordered arrangement of vacancies. Also shown for comparison are similar dependences for the disordered cubic phase according to the data obtained in [11]. TiO_y is taken as the structural unit for the calculation of the enthalpy of formation. The root-mean-square deviations of all the data do not exceed 3 kJ/mol for the enthalpy and 0.05 eV for the Fermi energy.

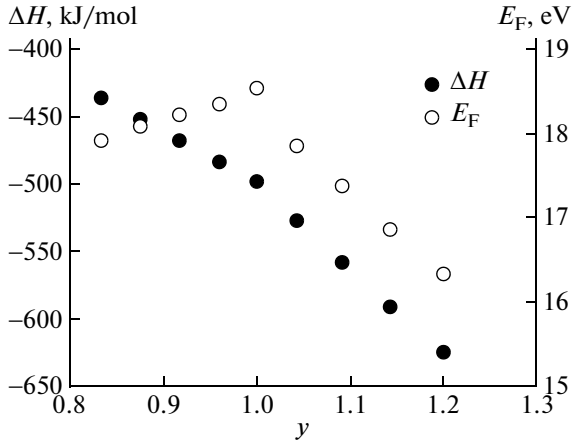

Fig. 8. Dependences of the enthalpy of formation and the Fermi energy on the composition y for the high-pressure phase with an ordered arrangement of vacancies. TiO_y is taken as the structural unit for the calculation of the enthalpy of formation. The root-mean-square deviations of all the data do not exceed 3 kJ/mol for the enthalpy and 0.05 eV for the Fermi energy.

region, the enthalpies of formation of the two phases coincide with each other.

In [9–12], it was shown that the ordered monoclinic phase is energetically more favorable than the disordered cubic phase. Nonetheless, the enthalpy of formation of hypothetical ordered phases, which are formed from the monoclinic phase by means of the complete removal of vacancies from one of the sublattices, turned out to be even somewhat higher than the enthalpy of formation of the high-pressure phase, although the difference in the enthalpies in this case lies within the standard deviation and varies in the range from 0 to 3.5 kJ/mol (0–0.7%). A variation in the lattice constant of the basic structure also did not lead to a substantial decrease in the energy of the ordered state as compared to the disordered state. Therefore, it should be concluded that the ordering according to the type of the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ superstructures is energetically unfavorable. A significant decrease in the total energy of the system due to the ordering occurs in the case when vacancies exist in both sublattices of the $B1$ basic structure, i.e., in the case of the formation of the monoclinic superstructure $Ti_5\blacksquare_1O_5\square_1$. The difference in the enthalpies of formation of the phases $Ti_5\blacksquare_1O_5\square_1$ and vacancy-free TiO, according to [11], is equal to 49.6 kJ/mol (9.7%).

The analysis of the dependences of the Fermi energy on the composition confirms the conclusion [11] that vacancies in the titanium sublattice decrease the Fermi energy to a considerably greater extent than vacancies in the oxygen sublattice. This is true not only for the boundaries but also for the entire region of homogeneity.

6. CONCLUSIONS

In this work, the electronic structure and stability of the disordered and ordered phases of titanium monoxide TiO_y with vacancies in only one of the sublattices have been investigated by the supercell method within the DFT-GGA approach using pseudopotentials. The calculation of the enthalpy of formation have demonstrated that, over the entire homogeneity region, except for its boundaries, the studied phases are energetically unfavorable as compared to the disordered cubic phase, in which vacancies are contained simultaneously in two sublattices. The removal of vacancies from one of the sublattices of titanium monoxide increases the energy of the compound. The ordering of vacancies remaining in the other sublattice according to the type of the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ superstructures gives no energy gain in comparison with their disordered state. The energy of the crystal significantly decreases due to the ordering according to the $Ti_5\blacksquare_1O_5\square_1$ type when vacancies are contained simultaneously in both sublattices.

In the case of a disordered arrangement of vacancies in the oxygen sublattice both in the absence and in the presence of vacancies in the titanium sublattice, there arises a small dip in the electron density of states at the Fermi level due to the redistribution of Ti $3d$ states. Upon ordering according to the type of the $Ti_5\blacksquare_1O_5\square_1$ superstructure, this dip increases and gives a pseudogap at the Fermi level. The ordering according to the $Ti_6O_5\square_1$ and $Ti_5\blacksquare_1O_6$ types does not lead to similar redistribution of electronic states.

ACKNOWLEDGMENTS

This study was supported by the Ural Branch of the Russian Academy of Sciences (project nos. 12-M-23-2001 and 13-3-NP-532).

REFERENCES

1. A. I. Gusev, A. A. Rempel, and A. Magerl, *Disorder and Order in Strongly Non-Stochiometric Compounds: Transition Metal Carbides, Nitrides, and Oxides* (Springer-Verlag, Berlin, 2001).
2. D. Watanabe, O. Terasaki, A. Jostsons, and J. R. Castles, in *The Chemistry of Extended Defects in Non-Metallic Solids*, Ed. by L. Eyring and M. O'Keefe (North-Holland, Amsterdam, The Netherlands, 1970).
3. A. A. Valeeva, A. A. Rempel', and A. I. Gusev, Inorg. Mater. **37** (6), 603 (2001).
4. A. A. Valeeva, A. A. Rempel, W. Sprengel, and H.-E. Schaefer, Phys. Rev. B: Condens. Matter **75**, 094107 (2007).
5. D. Watanabe, J. R. Castles, A. Jostsons, and A. S. Marlin, Acta Crystallogr. **23**, 307 (1967).
6. D. Watanabe, O. Terasaki, A. Jostsons, and J. R. Castles, J. Phys. Soc. Jpn. **25**, 292 (1968).
7. M. G. Kostenko and A. A. Rempel', Phys. Solid State **52** (4), 776 (2010).
8. M. G. Kostenko and A. A. Rempel', Phys. Solid State **53** (9), 1909 (2011).
9. D. A. Andersson, P. A. Korzhavyi, and B. Johansson, Phys. Rev. B: Condens. Matter **71** (14), 144101 (2005).
10. J. Graciani, A. Marquez, and J. F. Sang, Phys. Rev. B: Condens. Matter **72**, 054117 (2005).
11. M. G Kostenko, A. V. Lukoyanov, V. P. Zhukov, and A. A. Rempel', JETP Lett. **95** (12), 647 (2012).
12. M. G Kostenko, A. V. Lukoyanov, V. P. Zhukov, and A. A. Rempel', JETP Lett. **96** (8), 507 (2012).
13. A. Taylor and N. J. Doyle, in *The Chemistry of Extended Defects in Non-Metallic Solids*, Ed. by L. Eyring and M. O'Keefe (North-Holland, Amsterdam, The Netherlands, 1970), p. 523.
14. S. Bartkowski, M. Neumann, E. Z. Kurmaev, V. V. Fedorenko, S. N. Shamin, V. M. Cherkashenko, S. N. Nemnonov, A. Winiarski, and D. C. Rubie, Phys. Rev. B: Condens. Matter **56** (16), 10 656 (1997).
15. J. L. Murray and H. A. Wriedt, Bull. Alloy Phase Diagrams **8** (2), 148 (1987).
16. M. A. Korotin, A. V. Efremov, E. Z. Kurmaev, and A. Muves, JETP Lett. **95** (12), 641 (2012).
17. W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).
18. R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).
19. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
20. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A.D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samov, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter **21** (39), 395502 (2009).
21. M. D. Banus, T. B. Reed, and A. J. Strauss, Phys. Rev. B: Solid State **5** (8), 2775 (1972).
22. A. I Gusev and A. A. Valeeva, Phys. Solid State **45** (7), 1242 (2003).

Translated by O. Borovik-Romanova